AD-A008 438

THE THERMODYNAMICS OF THORIUM-OXYGEN AND URANIUM-OXYGEN SYSTEMS

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National Bureau of Standards

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER DNA 3546F	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER AD-A008 438
4. TITLE (and Subtitle) THE THERMODYNAMICS OF THORIUM-OXYGEN AND URANIUM-OXYGEN SYSTEMS		5. TYPE OF REPORT & PERIOD COVERED Final Report for Period 14 June 1973–30 June 1974
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Stanley Abramowitz		8. CONTRACT OR GRANT NUMBER(s) DNA MIPR 73-829 DARPA Order No. 1433 Program Code 3650
9. PERFORMING ORGANIZATION NAME AND ADDRESS National Bureau of Standards Washington, D.C. 20234		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS DNA Subtask M99QANHIO02-01
11. CONTROLLING OFFICE NAME AND ADDRESS Director Defense Advanced Research Projects Agency (DARPA) Washington, D.C. 20305		12. REPORT DATE 19 February 1975
		13. NUMBER OF PAGES 30
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Director Defense Nuclear Agency Washington, D.C. 20305		15. SECURITY CLASS (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Thermodynamics
Uranium-Oxygen Systems
Thorium-Oxygen Systems
Physical Chemistry

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The calorimetric, spectroscopic, and vapor pressure data for the uranium-oxygen and thorium-oxygen systems have been reviewed. Free energies of formation for the species UO, UO_2, ThO, and ThO_2 have been chosen. Tables of thermodynamic functions for these species are presented.

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THERMODYNAMICS OF THE URANIUM-OXYGEN SYSTEM

The vapor above uranium oxide condensed phases includes U, UO, UO_2, and UO_3. The composition of the vapor is strongly dependent upon the O/U ratio. In the three phase system $U(\ell)/UO_2(s)$ and vapor (O/U $\leq$ 1.7) the principal vapor phase species is UO with smaller amounts of U and UO_2 vapors. For UO_2 a congruent evaporation seems to predominate giving mostly UO_2 with about equimolar but much smaller quantities of UO and UO_3. For hyperstoichiometric urania (O/U > 2) UO_3 and UO_2 are the principal vapor phase species.

Uranium (s)

The vapor pressure of uranium has been studied over a wide temperature range most recently by Ackermann and Rauh (2) and Pattoret, Drowart and Smoes (2). Ackermann and Rauh have shown that the activity of the condensed phase varies from 1.0 downward as the electronegativity of the dissolved component increases. They give an expression for the vapor pressure of uranium

$$\log P_U \text{ (atm)} = (5.71 \pm 0.17) - (25,230 \pm 370)/T.$$

This yields a $\Delta H^\circ_{s\ 298} = 126.3 \pm 1.0$ kcal/mole. Pattoret et al (4) give

$$\log P_U \text{ (atm)} = (5.920 \pm 0.135) - (26,210 \pm 270)/T \text{ and}$$

$$\Delta H^\circ_{s\ 298} = 129.0 \pm 2.0 \text{ kcal/mole.}$$

These authors also summarize all the previous work on these systems by their laboratories and others. It is perhaps most significant that the vapor pressures that one will observe in these systems are a strong function of the container material or the dissolved components.

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$UO_2(s)/U(\ell)$

The partial pressures of the species are determined by mass spectroscopic measurements, while the total pressures have been measured by both effusion and transpiration techniques. The total mass spectroscopic instrument sensitivity to a particular gas phase species has to be known in order to compute the partial pressures

$$Pi = I^+_{(i)} T/\sigma_i \nu_i = I^+ T/k_i$$

where σ_i and ν_i are the cross-section for ionization by electrons of a given energy and the detector sensitivity to the species of interest. Various assumptions have been made concerning these k_i quantities. Ackermann et al (3) in their work on the $U(\ell)/UC_2(s)$ system used equal sensitivities for $U(v)$, $UO(v)$ and $UO_2(v)$. A recent work by Blackburn and Danielson (4) has advocated values of 0.66, 1.29, and 0.31 for the product of multiplier yield and partial relative ionization cross-section for U, UO and UO_2 using a 10 eV ionizing electron beam. (For this energy beam these partial relative ionization cross-sections are equal to the total relative ionization cross-sections).

The pressure of uranium species above of $U(\ell)$, $UO_2(s)$ is given by

$$\log P_e = (7.25 \pm 0.15) - (27.020 \pm 250)/T \text{ (for } 1580-2400°K)$$

by Ackermann et al (1). Pattoret et al (3) report a pressure of UO given by $\log P = 8.19 - 28,020/T$ in the temperature interval of 1700 - 2150°K.

There is considerable evidence that the system $UO_2(s)/U(\ell)$ is far from ideal. Therefore the activities of the condensed phases cannot be assumed to be unity, for the process

$$U_{(\ell)} + UO_{2(s)} = 2UO \text{ (g)}.$$

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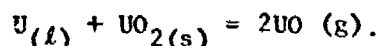
Consequently the measurement of thermal functions for this system has
to be done using gas phase equilibria where activity coefficients can
be assumed to be unity. Ackermann et al (3) measured the gas phase
equilibria

$$U_{(g)} + UO_{2(g)} = 2UO_{(g)}$$
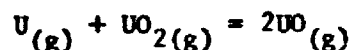
and from the known free energy functions of $UO_2(g)$ (this will be discussed
later) and $U_{(g)}$ and the measured equilibrium constant as a function of
temperature.

$$K = P^2_{UO}/P_U P_{UO_2}$$

where, $\log K = (1.268 \pm 0.05) + (2091 \pm 117)/T$

They computed $\Delta G_f^\circ (UO,g)$

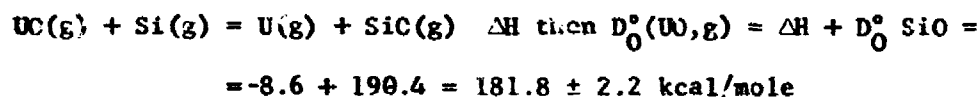$$\Delta G_f^\circ (UO,g) = 1/2 \Delta G_f^\circ (UO_2,g) + 1/2 \Delta G_f^\circ (U,g) - 1/2 R'T \log K$$
$$= -7,800 - 13.84T.$$

It should be, of course, noted that this measurement of K required a
knowledge of the k_i's. Ackermann et al (3) assumed that k_i of the various
species were equal to each other. Incorporation of Blackburn and
Danielson's data (4) for partial relative ionization cross-sections would
change the measured equilibrium constant by almost a factor of 1/8. This
would have the effect of decreasing the ΔS_f° of UO(g) from 13.84 e.u. to
about 11.78 e.u. without affecting the ΔH° term. Other potential sources
of error are the $\Delta G_f^\circ UO_2(g)$ and $\Delta G_f^\circ U(g)$. As will be seen later in this
report an uncertainty in the entropy of formation, $\Delta S_f^\circ UO_2 (g)$ is not
unlikely. This error would contribute an uncertainty of 1.5 e.u. to
the $\Delta S_f^\circ UO(g)$.

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The D_0° computed from the ΔH_f° of UO determined by Ackermann et al (3) is

$$D_0^{\circ} = \Delta H_s(U,g) + 1/2\ D_0^{\circ}O_2 - \Delta H_f(UO)$$
$$= 115.4_3 + 59.0 + 7.8 = 182.2 \pm 3\ \text{kcal/mole.}$$

(It should of course be noted that a correction for ΔH_s and ΔH_f UO to 0 K has not been made, however these corrections should go in the same direction and tend to cancel each other). Pattoret et al (5) determined a D_0° for UO(g) from the isomolecular exchange reaction

$$UC(g) + Si(g) = U(g) + SiC(g) \quad \Delta H \text{ then } D_0^{\circ}(UO,g) = \Delta H + D_0^{\circ}\ SiO =$$
$$= -8.6 + 190.4 = 181.8 \pm 2.2\ \text{kcal/mole}$$

which is in excellent agreement. Unfortunately no relative ionization cross-sections were quoted in this work. Although in a later work (2) the authors give k_i's of 1.15, 0.80, and 0.55 for U, UO and UO_2 respectively. These numbers would give an overall correction of 0.99 to the equilibrium constants given by Ackermann et al (3).

A computation of ΔS_f° of UO from spectroscopic data requires a knowledge of the electronic levels of UO. No spectroscopic assignment for the electronic energy levels of UO is available in the literature. The infrared spectrum of matrix isolated UO has been observed by several workers. Using this vibrational frequency and the estimated bond distance of about 1.75Å one can compute the S_{2000K}° for UO without electronic contribution of 73.4 e.u. From this value and those of liquid uranium and molecular oxygen an entropy of formation of UO (defined by the equation $U(\ell) + 1/2O_2 = UO(g)$ (2000K)) of 8.9 e.u. mole^{-1} is computed. This value is considerably less than the 13.84 e.u. quoted by Ackermann (or for that

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matter the 11.78 obtained by using Blackburn and Danielson's k_i's).
Unfortunately there exists no easy way to remedy this situation without
the necessary spectroscopic data. The ΔS_f° of 13.84 can be rationalized
to the observed data of 8.1 e.u. if one has a ground state with a
degeneracy of about 13. (The $\Delta S_f^\circ = 11.78$ gives a ground state degeneracy
of about 5).

The partial pressures of the U, UO, UO_2 species above the three
phase system $U(\ell)/UO_{2-x(s)}$ have been given by Ackermann et al (3) as

$$\log P_U = (5.21 \pm 0.14) - (25,640 \pm 300)/T$$

$$\log P_{UO} = (7.11 \pm 0.14) - (26,880 \pm 300)/T$$

$$\log P_{UO_2} = (7.74 \pm 0.14) - (30,180 \pm 300)/T.$$

These equations were derived from their measurements in the temperature
range of 1820 - 2490 K assuming equal $\sigma_i v_i$ for the three species.
Pattoret et al (5) have also observed that the $I^+_{UO}/I^+_U/I^+_{UO_2}$ is
about 10/1/1 for this system. Pressure ratios of about 10/1/1 are
obtained from Ackermann et al whereas ratios of about 12.5/0.87/1.82
and about 7.75/1.52/3.23 are obtained using the $\sigma_i v_i$ given by Pattoret
et al (5) and Blackburn and Danielson (4) respectively. The partial
pressures computed using the three sets of $\sigma_i v_i$ are given in the
following table. (The data for P_e of Ackermann (3) at 2000 K are
used in order to facilitate a direct comparison.)

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	P_U (atm)	P_{UO} (atm)	P_{UO_2} (atm)	$P_U/P_{UO}/P_{UO_2}$
ARC(3)	2.45×10^{-8}	4.68×10^{-7}	4.47×10^{-8}	1/18.9/1.82
PDS(5)	2.13×10^{-8}	5.79×10^{-7}	8.13×10^{-8}	1/27.2/3.82
BD (4)	3.72×10^{-8}	3.59×10^{-7}	1.44×10^{-7}	1/9.65/3.87

It should be noted that the partial pressure ratios are significantly different from the three sets of $\sigma_i \gamma_i$ used.

The measurements of Pattoret et al (5) give a pressure of UO about 2.4 times greater than those of Ackermann et al (3). The $\sigma_i \gamma_i$ used by the three workers are given below together with the K_p computed.

relative $\sigma_i \gamma_i$	U	UO	UO_2	Ke
PDS (5)	1.15	0.80	0.55	0.988
ARC (3)	1	1	1	1
BD (4)	0.66	1.29	0.31	0.123

for $U_{(g)} + UO_{2(g)} = 2UO_{(g)}$
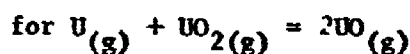
$$K_p(T) = \left[\frac{I^+_{UO^2}/(\sigma\gamma)_{UO^2}}{I^+_{UO_2}/(\sigma\gamma)_{UO_2} I^+_{U}/(\sigma\gamma)_{U}} \right] K_e$$

At 2000K the pressures given by Ackermann et al (3) and Pattoret et al (5) are

$$\begin{aligned}
ARC(3)P_{UO} &= 4.68 \times 10^{-7} \\
P_{UO_2} &= 4.47 \times 10^{-8} \qquad P_e = 5.495 \times 10^{-7} \\
P_U &= 2.45 \times 10^{-8} \\
PDS(5)P_{UO} &= 1.12 \times 10^{-6}
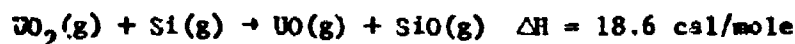\end{aligned}$$

Stoichiometric UO_2

The vapor pressure above stoichiometric UO_2 has been measured by several workers (6-10) using both mass transpiration and effusion techniques. The congruently evaporating compositions of urania have also been systematically measured as a function of temperature by analysis of the residues after appreciable Knudsen effusion loss. These residu s become increasingly hypostoichiometric with temperature varying from $UO_{2.000}$ to $UO_{1.940}$ in the 1940 - 2386 K temperature interval (9). It has also been suggested that a significant partial pressure of UO and UO_3 is present even at lower temperatures, UO_3 becoming predominant to the UO as the temperature increases (9).

The results of some of the more recent experiments are given below. The vapor pressure of the uranium bearing species is represented by the equation

$$\Delta G = -RT \ln P_{(U)} = \Delta \dot{H} - T \Delta \dot{S}$$

$$\text{or} \quad \log P(atm) = \frac{-\Delta \dot{H}}{R'T} + \frac{\Delta \dot{S}}{R'}$$

ΔH	ΔS	method	temp. range	ref.	P_{2200K}
137.1	36.4	mass effusion	1600-2200	AGT(6)	2.17×10^{-6}
147.1	42.2	" "	1920-2220	Ivanov(10)	4.08
147.8	42.0	" "	2200-2800	Ohse(8)	3.14
141.2	39.4	mass spect.	1890-2420	PDS '67(5)	3.84
143.1	39.4	transpiration	2085-2705	TH (7)	2.49
134.1	34.5	" "	2000-2940	Alexander (11)	1.66

By observing the equilibrium ion currents for the reaction

$$UO_2(g) + Si(g) \rightarrow UO(g) + SiO(g) \quad \Delta H = 18.6 \text{ cal/mole}$$

and from a knowledge of D_0° $UO(g)$ and $SiO(g)$. Pattoret et al (5) computed a D_0° of UO_2 of 353.6 ± 3.2 kcal/mole,

$$D_0^\circ \, UO_2 = \Delta H + D_0^\circ \, SiO + D_0^\circ \, UO$$
$$= 18.6 + 190.4 + 181.8 = 353.6.$$

This value is in good agreement with 353.2 (14.9eV) given by Ackermann Gilles and Thorn (6). These workers used the $UO_2(g)$ equilibria coupled with the data for $UO_2(s)$ given by Kelley (Bur. Mines Bull. 476, 1909) and estimated thermodynamic data for the vapor. Pattoret et al (5) obtained a value of 352.5 kcal/mole from the $UO_2(s) = UO_2(g)$ using

$$\Delta H_f^\circ \,_{298} \, UO_2(s) = -259.5 \text{ kcal/mole}$$
$$\Delta H_s^\circ \,_{298} \, UO_2 = 125 \text{ kcal/mole}$$

then

$$UO_2(s) = UO_2(g) \quad \Delta H_f^\circ = 152.5$$
$$D_0^\circ(UO_2 g) = -\Delta H_f(UO_{2,g}) + \Delta H_s \, U_{(s)} + D_0^\circ \, O_2$$
$$= (259.5 - 152.5) + 129.0 + 117 = 353 \text{ kcal/mole}$$
$$UO_2(g) = U(g) + 2O(g) \quad D_0^\circ \, UO_2.$$

Therefore since both gas phase equilibria coupled with assumed previously determined dissociation energies agree well with ΔH for $UO_{2(s)}$ = $UO_{2(g)}$ coupled with $\Delta H_s U$ and $D_0^\circ O_2$ for the determination of $D_0^\circ(UO_2)$ one can have a degree of confidence of the thermal functions for UO_2 determined by the congruent vaporization of stoichiometric urania.

It has been noted by Tetenbaum and Hunt (7) that the pressures derived from effusion measurements on stoichiometric urania by Ackermann et al (6) and Ohse (8) are higher at temperatures above 2350C than those obtainable using the transpiration methods. The original proposal by Ackermann et al of a UO_2 dimer is not consistent with the pressure measurements of Tetenbaum and Hunt. Mass spectroscopic measurements have not been successful in finding a UO_2 dimer. Rather the positive curvature in the vapor pressure with temperature above 2350 C is probably caused by a departure from molecular flow in the Knudsen cell. Edwards et al (9) have suggested increased pressures of UO_3 in order to reach the proper UO_{2-x} for the higher temperatures. This explanation has also been rejected by Tetenbaum and Hunt since $\ln P$ vs $1/T$ is a straight line over the range of 2080-2705 K for various UO_{2-x} specimens.

The free energy of formation, $\Delta G_f^\circ\ UO_2(g)$ can in principle be derived from the vapor pressure measurements above stoichiometric UO_2 assuming the principal reaction is

$$UO_2(s) \to UO_2(g) \qquad \Delta G_s UO_2(s) = -R'T \log P.$$
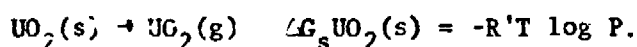
This quantity coupled with $\Delta G_f^\circ\ UO_2(s)$ then yields $\Delta G_f^\circ\ UO_2(g) =$ $\Delta G_f\ UO_2(s) + \Delta G_s\ UO_2(s)$.

If one inspects table 3 which gives the $\Delta G_s^\circ\ UO_2(s) = \Delta H_{(s)}^\circ - T\Delta S_{(s)}^\circ$ one finds the ΔS terms vary from 42.4 to 34.5 cal/mole K. with an average deviation of about 2.4 cal/mole K. The uncertainty in the entropy of this process will be reflected in the computation of ΔS_f° $UO_2(g)$. Using Ackermann et al (6) vapor pressure data one obtains $\Delta S_f^\circ = -4.24$ e.u, the data of Pattoret et al (5) gives $\Delta S_f^\circ = -1.24$

as does the data of Tetenbaum and Hunt (7). Perhaps this latter value
is expected to be more reliable since the method of mass transpiration
over a long temperature range is in agreement with mass spectroscopic
observations over a smaller and to an extent overlapping temperature
range.

Using the vibrational assignment for UO_2 given by Gabelnik et al
(12) and Abramowitz et al (13) namely $\nu_1 = 765.9$, $\nu_3 = 776.1$ and
$\nu_2 = 81$ cm^{-1} for a linear UO_2 molecule with a r U–O = 1.75 Å a S°_{2000K}
= 92.3 cal mole^{-1}, $^{-1}$ is computed. Small variations of r will not
significantly effect the computed functions. Coupling this with S°_{2000}
U(ℓ) = 72.53 and S°_{2000} O_2 = 64.18 one obtains a ΔS_f $UO_2(g)$ = -4.41 cal
mole^{-1}K^{-1} in excellent agreement with ΔS°_f = -4.24 given by Ackermann
et al (6) and in good agreement with ΔS°_f = -1.24 given by Tetenbaum and
Hunt (7) and Pattoret et al (5). It should of course be noted that
for the purposes of this computation of S°_{2000K} of UO_2 a singlet ground
state was assumed and any contribution to the entropy from low lying
electronic states has been neglected. (There have not been any
electronic spectra of $UO_2(g)$ or matrix isolated UO_2 observed and
analyzed).

The ionization potential of U, UO and UO_2 have been measured using
the RPD (retarding potential difference) method by Mann (14). He has
given values of 6.1, 5.7, and 5.5 eV for the ionization potentials of
U, UO, UO_2 respectively. These values which are probably good to about
0.1 eV have been accepted by other workers in the field. These ionization
potentials coupled with the ΔH_f UO and ΔH_f UO_2 then can be used to

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estimate exothermicities of reactions such as:

Reaction	eV
$U(s) + O_2 \rightarrow UO_2(g)$	-5.27
$U(s) + \frac{1}{2}O_2 \rightarrow UO(g)$	-0.34
$U(s) \rightarrow U(g)$	+5.00
$U(g) + O_2 \rightarrow UO_2(g)$	-10.27
$U(g) + O_2 \rightarrow UO_2^+ + e$	-4.77
$U(g) + \frac{1}{2}O_2 \rightarrow UO(g)$	-5.34
$U(g) + O \rightarrow UO(g)$	-7.90
$U(g) + O \rightarrow UO^+(g) + e$	-2.20
$U(g) + \frac{1}{2}O_2 \rightarrow UO^+ + e$	+0.3
$U(g) + O_3 \rightarrow UO_2 + O$	-.71
$U(g) + O_3 \rightarrow UO_2^+ + O + e$	1.21
$U(g) + O_3 \rightarrow UO + O_2$	-4.34
$U(g) + O_3 \rightarrow UO^+ + O_2$	+1.3
$U(g) + N_2O \rightarrow UO + N_2$	-4.49
$U(g) + N_2O \rightarrow UO^+ + N_2 + e$	+1.21

The thermodynamic functions for UO and $UO_2(g)$ are given in Tables 1 and 2. These computations are done assuming singlet ground states for both species and no allowance is made for any possible contribution to these functions from any excited electronic states. This was done in this manner since there are no experimental determinations for the electronically excited levels of UO and UO_2.

TABLE 1. THERMODYNAMIC FUNCTIONS FOR UO(g)

PF APPROXIMATED AS A(PF)+2/(1 E)+2 2.93574E-7 STATE 1

T	CP	H-HC	S	-(G-HC)/T
K	CAL/K MOL	CAL/MOL	CAL/K MOL	CAL/K MOL
298.15	7.57705	2119.57	57.2717	50.1626
300	7.58519	2133.59	57.3186	50.2066
400	7.96505	2912.23	59.5559	52.2753
500	8.2356F	3723.29	61.3646	53.9181
600	8.41637	4556.49	62.8532	55.2891
700	8.54034	5400.69	64.1905	56.4695
800	8.62786	6253.34	65.3369	57.5075
900	8.69151	7129.47	66.357	58.4354
1000	8.7391	8001.11	67.2753	59.2742
1100	8.77559	8876.92	68.11	60.0401
1200	8.8042	9755.97	68.8749	60.7449
1300	8.82707	10637.6	69.5905	61.3978
1400	8.84569	11521.2	70.2354	62.0059
1500	8.86105	12406.6	70.9462	62.5752
1600	8.874	13293.8	71.4155	63.1102
1700	8.88497	14181.3	71.9565	63.6149
1800	8.89441	15070.3	72.465	64.0926
1900	8.90262	15960.2	72.9461	64.546
2000	8.90983	16850.8	73.4029	64.9775
2100	8.91622	17742.1	73.8378	65.3891
2200	8.92193	18634.	74.2527	65.7827
2300	8.92707	19526.5	74.6496	66.1596
2400	8.93175	20419.4	75.0294	66.5213
2500	8.93602	21312.9	75.3941	66.869
2600	8.93995	22206.6	75.7447	67.2037
2700	8.94355	23100.9	76.0821	67.5263
2800	8.94697	23995.3	76.4074	67.8377
2900	8.95013	24890.2	76.7215	68.1386
3000	8.9531	25785.3	77.0249	68.4298
3100	8.95591	26680.2	77.3185	68.7119
3200	8.95857	27576.5	77.6029	68.9852
3300	8.9611	28472.5	77.8786	69.2506
3400	8.94352	29369.7	78.1462	69.5083
3500	8.96584	30265.2	78.406	69.7585
3600	8.96806	31161.9	78.6586	70.0025
3700	8.97021	32059.8	78.9044	70.2398
3800	8.97228	32955.9	79.1436	70.471
3900	8.97429	33853.3	79.3767	70.6963
4000	8.97623	34750.8	79.6039	70.9162
4100	8.97812	35648.5	79.8254	71.1305
4200	8.97997	36546.4	80.0419	71.3404
4300	8.98177	37444.5	80.2532	71.5452
4400	8.98353	38342.8	80.4597	71.7455
4500	8.98524	39241.2	80.6616	71.9414
4600	8.98695	40139.8	80.8591	72.1331
4700	8.98561	41038.6	81.0524	72.3208
4800	8.99024	41937.5	81.2417	72.5047
4900	8.99185	42836.7	81.4271	72.6849
5000	8.99343	43735.9	81.6087	72.8615
5100	8.995	44635.3	81.7868	73.0348
5200	8.99654	45534.9	81.9615	73.2048
5300	8.99806	46434.6	82.1329	73.3714
5400	8.99957	47334.5	82.3011	73.5354
5500	9.00105	48234.6	82.4662	73.6963
5600	9.00253	49134.7	82.6284	73.8543
5700	9.00399	50035.1	82.7877	74.0097
5800	9.00544	50935.5	82.9443	74.1623
5900	9.00687	51836.2	83.0983	74.3125
6000	9.00829	52736.9	83.2497	74.4602

MOLECULAR WEIGHT= 254.07
MOLECULAR CONSTANTS ARE LISTED AS:
LEVEL:1,E2,E3,TF,T,FF,AI,FHEF,IS,MULTIPLICITY+100

1 520 0 0 .3668 0 2.93574E-7 1 2

TABLE 2. THERMODYNAMIC FUNCTIONS FOR UO$_2$(g)

T	(F-H0)/T	(H-H0)/T	S	CP
298.15	-55.0126	10.5706	65.5832	12.2796
300	-55.078	10.5812	65.6592	12.2967
400	-58.1969	11.1133	69.3102	13.0742
500	-60.7262	11.5608	72.2872	13.5907
600	-62.8679	11.9293	74.7472	13.9298
700	-64.7303	12.2324	76.9627	14.15F1
800	-66.3806	12.4837	78.8643	14.3171
900	-67.8635	12.6941	80.5575	14.4314
1000	-69.2104	12.8722	82.0826	14.5156
1100	-70.4646	13.0247	83.4693	14.5709
1200	-71.5827	13.1564	84.7401	14.6295
1300	-72.6414	13.2713	85.9127	14.6686
1400	-73.6297	13.3723	87.0009	14.7
1500	-74.5542	13.4617	88.016	14.7256
1600	-75.4255	13.5413	88.9671	14.7467
1700	-76.2469	13.6126	89.5617	14.7642
1800	-77.0256	13.6772	90.706	14.779
1900	-77.7699	13.7355	91.5054	14.7916
2000	-78.4755	13.7886	92.2446	14.8024
2100	-79.1497	13.8371	92.8568	14.8117
2200	-79.7945	13.8816	93.676	14.8197
2300	-80.4125	13.9225	94.335	14.8268
2400	-81.0058	13.9603	94.9661	14.833
2500	-81.5764	13.9953	95.5718	14.8385
2600	-82.126	14.0279	96.1538	14.8434
2700	-82.6559	14.0582	96.7141	14.8478
2800	-83.1677	14.0864	97.2542	14.8517
2900	-83.6625	14.1129	97.7754	14.8552
3000	-84.1414	14.1377	98.2791	14.8593
3100	-84.6053	14.161	98.7663	14.8612
3200	-85.0553	14.1829	99.2382	14.8637
3300	-85.492	14.2036	99.6956	14.8662
3400	-85.9163	14.2231	100.139	14.8683
3500	-86.3289	14.2415	100.57	14.8703
3600	-86.7303	14.259	100.989	14.8721
3700	-87.1213	14.2756	101.397	14.8739
3800	-87.5022	14.2914	101.794	14.8754
3900	-87.8736	14.3064	102.18	14.8768
4000	-88.236	14.3207	102.557	14.8781
4100	-88.5898	14.3343	102.924	14.8794
4200	-88.9353	14.3473	103.283	14.8805
4300	-89.2731	14.3597	103.633	14.8816
4400	-89.6033	14.3716	103.975	14.8826
4500	-89.9264	14.3829	104.309	14.8835
4600	-90.2427	14.3935	104.636	14.8844
4700	-90.5524	14.4043	104.957	14.8852
4800	-90.6557	14.4143	105.27	14.8859
4900	-91.152	14.4239	105.577	14.8867
5000	-91.4465	14.4332	105.878	14.8873
5100	-91.7204	14.4421	106.173	14.888
5200	-92.0109	14.4507	106.462	14.8886
5300	-92.2642	14.4589	106.745	14.8891
5400	-92.5566	14.4669	107.024	14.8897
5500	-92.5960	14.4746	107.297	14.8902
5600	-93.063	14.482	107.565	14.8907
5700	-93.3394	14.4892	107.829	14.8911
5800	-93.5915	14.4961	108.088	14.8916
5900	-93.8393	14.5028	108.342	14.892
6000	-94.0931	14.5093	108.592	14.8924

FUSO	MELT	FUSO	MELT
765.4	1	776.1	1
P1	0	0	0

MOLECULAR WEIGHT 270.08
SYMMETRY 2
MOMENT OF INERTIA 98
TYPE C
END OF RUN

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SECTION 2

THERMODYNAMICS OF THE THORIUM-OXYGEN SYSTEM

The thorium-oxygen system has been studied by mass spectroscopic techniques by several workers (1-5). A summary and review of some of the older works not referenced in this report are also available (6). The method used in studying these systems is to measure the vapor pressure of the thorium species effusing from a Knudsen cell by weight gain of a circular disc target. The pressures are measured over $ThO_2(s)$ and the 3 phase system $Th(\ell)/ThO_2(s)/vapor$, or in the lower temperature regimes $Th(s)/ThO_2(s)/vapor$. Partial pressures of the species are determined mass spectrometrically. This requires assumptions of cross sections and detector sensitivities for the various species.

In the case of vaporization from $ThO_2(s)$ two processes are important

(1) $ThO_2(s) \rightarrow ThO_2(g)$

(2) $ThO_2(s) \rightarrow ThO(g) + O(g)$.
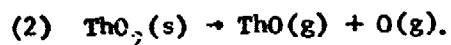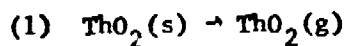
The assumptions are made that the mass spectrometric peak intensities of the $ThO^+(g)$ and $ThO_2^+(g)$ ions can be related to pressures and vaporization of reaction (2) is congruent. Thermodynamic functions of $ThO(g)$ and $ThO_2(g)$ can be obtained from a knowledge of $\Delta G_f(T)$ of $ThO_2(s)$. (This assumes that $a_{ThO_2(s)} = 1$).

For a study of either the three phase system $ThO_2(s)/Th(\ell)$ or the $ThO_2(s)/Th(s)$ for which the principal vaporization can be represented by

$$\tfrac{1}{2}ThO_2(s) + \tfrac{1}{2}Th(s) \rightarrow ThO(g)$$

$$\tfrac{1}{2}ThO_2(s) + \tfrac{1}{2}Th(\ell) \rightarrow ThO(g)$$
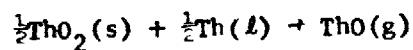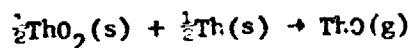
one must know the activity of $ThO_2(s)$ and $Th(s,\ell)$. It has been shown

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that prolonged vaporization of ThO from this system at temperature
below 2400K does not appreciably alter the stoichiometry of the ThO_2(s)
phase (7). This then allows one to assume unit activity for both Th
(s,ℓ) and ThO_2(s). Therefore combining the pressures of ThO obtained
and the thermal properties of ThO_2(s) and Th(s,ℓ), allows a determination
of ΔG_f° of ThO(g). Ackermann and Rauh (3) give ΔG_f°ThO(g) = -16,500-12.15T
kcal mol^{-1} [2400-2800 K]. Hildenbrand and Murad (5) give an expression
for $\log_{10} P_{ThO}$ = (8.386 ± 0.164) -(30,480 ± 306)/T which is in experimental
agreement with the pressures given by Ackermann and Rauh. These values
are also in excellent agreement with the pressure of ThO(g) given in
reference 1 for 2369K. (The pressure over ThO_2(g)/Th(ℓ) was only given
at this temperature for this system by these workers.)

This indicates a ΔS_f° of ThO(g) of 12.15 entropy units. This value
is in agreement with the entropy computed for ThO(g) using the known
spectroscopic states and the measured entropy for Th(ℓ).

Estimates of the electronic contributions to S_{2000K}° of ThO have been
made in the past by equating this entropy with that of S_{2000K}° of Th(III).
This method gives an absolute entropy of 80.5 cal/mole °K compared with
an S_{2000K}° of 73.9 cal/mole K using molecular constants of the known
electronic states of ThO(g). The latter value in good agreement with a
second law treatment of the vaporization data for the ThO_2(s)/Th(s,ℓ)
system.

The dissociation energy of ThO may be obtained via several cycles.
Ackermann and Rauh (3) considered the isomolecular exchange

$$YO(g) + Th(g) \rightarrow ThO(g) + Y(g)$$
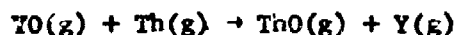
and from the known thermodynamic functions of $YO(g)$, $Th(g)$ and $Y(g)$ were
able to obtain D_0° of ThO. They also obtained D_0° $ThO(g)$ and ΔH_0° of ThO
obtained from the study of the reaction

$$\tfrac{1}{2}Th(s,\ell) + \tfrac{1}{2}ThO_2 \text{ (s)} \rightarrow ThO(g), \quad \Delta Hs \text{ Th(s) and } \tfrac{1}{2}D_0^\circ \text{ of } O_2 \text{ via the cycle}$$

$$Th(s) + \tfrac{1}{2}O_2 \rightarrow ThO \qquad \Delta H_0^\circ$$

$$ThO \rightarrow Th(g) + O(g) \qquad D_0^\circ.$$
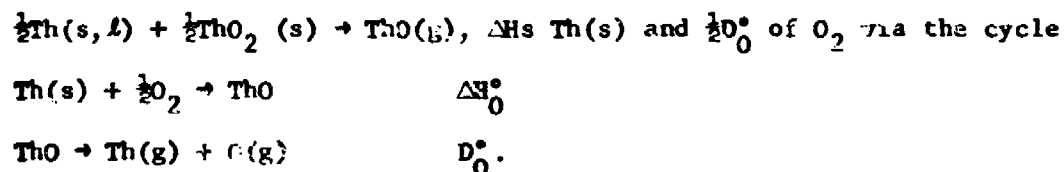
The ΔH_0° for $ThO(g)$ obtained by the second and third law methods
are in rather good agreement. The thermal functions for $ThO(g)$ were
generated using the known spectroscopic data for ThO. The values for
$Th(s,\ell)$ were taken from Rand's evaluation (8) as given by Ackermann
and Rauh (3).

Hildbenbrand and Murad (5) also obtained D_0° of ThO via an isomolecular
exchange reaction

$$ThO(g) + Si(g) \rightarrow Th(g) + SiO(g)$$

and a study of the $Th(s) + ThO_2(s)$ system. The D_0° recommend by these two
groups are within experimental error. A value of 8.78 ± 0.13 eV is given
in (4) while 9.0 ± 0.1 eV is recommended in (3). Even this small
difference represents to some extent the different choice of thermal
functions for $ThO_2(s)$ by these two different laboratories.

From a knowledge of ΔG_f° of $ThO_2(s)$ one can obtain ΔH_f° (ThO_2,g) since

$$log_{10} P(ThO_2,g) = -35,070/T + 7.96$$

over $ThO_2(s)$ and ΔG_f° $ThO_2(s) = -292,600 + 43.66\ T$

$$\Delta G_f^\circ\ ThO_2(g) = -132,100 + 7.23\ T.$$

From a knowledge of ΔS° for this process coupled with frequencies of $ThO_2(g)$ determined by several workers (assuming a value of ν_2), and the ThO_2 angle and bond distances one can compute S° for ThO_2 which can be compared with values obtained experimentally for the $ThO_2(s) \rightarrow ThO_2(g)$ process.

Using the entropy for $Th(\ell,s)$ derived from the calorimetric data (12) by Rand (8) and the entropy of molecular oxygen (13), one computes and entropy for $ThO_2(g)$ of $S_{2600}^\circ = 92.8$ e.u., (since $\Delta G_f(ThO_2,g) = -132,100 + 7.23\ T$ for the temperature interval of 2400-2800 K). A computation of the entropy of ThO_2 using either of the recently observed vibrational spectra for the stretching modes of ThO_2 coupled with the molecular geometry determined by isotopic shifts for $Th^{16}O_2$ and $Th^{18}O_2$ (14,15) yield values of 97.5 eu. for $\nu_2 = 81$ cm^{-1} and 96.7 e.u. for $\nu_2 = 125$ cm^{-1}. The former value was chosen from a determination of 81 cm^{-1} for the bending mode of UO_2. Lirevsky estimated 125 cm^{-1} for ν_2 from a weak combination band observed in the infrared spectrum. Repeated efforts by the author have not yielded an experimental determination of ν_2 even though the spectrum could be observed down to about 60 cm^{-1}. In any event this difference (4 to 5 eu) between the calculated entropy and the thermodynamically derived entropy is not easily explainable.

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To reduce the calculated entropy by 4 would require a change of the bending frequency to a very high value, hence the derived entropy probably is too low by at least 2 entropy units, or more likely 3 units.

A discrepancy of about 12 kcal/mole exists between the determination of the ΔH_0° $ThO_2(g)$ using the second and third law methods. There is no apparent problem in any of the experiments used to generate the vapor pressure, heat capacity of the solid phase, and spectroscopic data used for these determinations. Examination of $ThO_2(s)$ after prolonged vaporization indicated very little departure from stoichiometry. There-fore assumptions of unit activity seem to be justified. An investigation of the temperature variation in the equilibrium constants of the reactions

$$\tfrac{1}{2}Th(g) + \tfrac{1}{2}ThO_2(g) \rightarrow ThO(g)$$

and

$$ThO_2(g) \rightarrow ThO(g) + O(g)$$
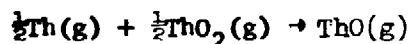
coupled with the known thermodynamic functions for $Th(g)$, $ThO(g)$ and $O(g)$ might be helpful in providing another path to the determination of ΔG_f° (ThO_2,g) from which ΔH_f° could be computed.

The $\Delta H_f^\circ,T$ given by Ackermann and Rauh (1,3) have been reduced to ΔH_{f0}° using the thermodynamic function for $(G-H_0^\circ)/T$ for the species $Th(s,\ell)$, O_2 and $ThO_2(g)$.

This computation gives

$$\Delta H_f^\circ \; ThO_2(g) = -105.4 \; kcal/mole$$

$$\Delta H_f^\circ \; ThO(g) = -6.15 \; kcal/mole.$$

This enables an estimate of D_0° of ThO_2

$$D_0^\circ = \Delta H_{s0}^\circ \; (Th,s) + D_0^\circ \; (O_2) - \Delta H_f^\circ \; (ThO_2,g) = 142.7 + 118 + 105.4$$

$$= 366.1 \; kcal/mole \; or \; 15.9 \; eV/mole.$$

The I.P. Th, I.P. ThO, and I.P. ThO_2 have been given as 5.9, 6.1 and 8.7 eV, respectively in (3). These values which have estimated uncertainties of ± 0.2 eV are in agreement with the recent results given by reference 4 of 6.0 and 8.0 ± 1 eV for ThO and ThO_2 and some yet unpublished results on the optical spectra of Th respectively. (It should of course be noted that thermal population of electronic states may contribute some error to these values.) These ionization potentials coupled with ΔH_f° of ThO and ThO_2 then can be used to estimate exothermicities of reactions such as:

Reaction	eV
$Th + O \rightarrow ThO^+ + e$	-2.9
$Th + O_2 \rightarrow ThO_2^+ + e$	-2.1
$Th + O_2 \rightarrow ThO + O$	-3.9
$Th + O_3 \rightarrow ThO + O_2$	-7.4
$Th + O_3 \rightarrow ThO^+ + O_2 + e$	-1.3
$Th + O_3 \rightarrow ThO_2^+ + O + e$	-0.5

These quantities were calculated using the following energies:

Reaction	eV
$Th \rightarrow Th^+ + e$	5.9
$Th \rightarrow ThO^+ + e$	6.1
$ThO_2 \rightarrow ThO_2^+ + e$	8.7
$ThO \rightarrow Th + O$	9.0
$ThO_2 \rightarrow Th + 2O$	15.9
$Th(s) + O_2 \rightarrow ThO_2(g)$	-5
$Th(s) + \frac{1}{2}O_2 \rightarrow ThO$	-0.22
$O_2 \rightarrow 2O$	5.1
$O_3 \rightarrow O_2 + O$	1
$Th(s) \rightarrow Th(g)$	6.2

The thermodynamic functions of ThO and ThO_2 are appended in tables 3, 4, and 5. It should be noted that all twelve known electronic states of ThO have been included in this calculation. The multiplicity of the lowest excited state has been taken as 2 in this computation. Wentink et. al. (11) have suggested that this state might have a degeneracy of $6(^3\Delta)$ from a comparison of the levels of TiO, H_fO and ThO. This suggestion has apparently been accepted in reference 3 and those thermal functions reflect this assignment. This has the effect of increasing the S°_{2600} of ThO(g) by about 1.13 e.u. Tables 4 and 5 give thermodynamic functions for ThO_2, (g) using both vibrational assignments for v_2 of 81 and 125 cm^{-1} and $\alpha = 115^\circ$, $r = 1.75$ Å. Small variations of α and r will not significantly effect the computed entropy. The choice of $v_2 = 125$ cm^{-1} is probably to be preferred at this point since it reduces the discrepancy between a second and third law treatment of the available data.

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TABLE 3. THERMODYNAMIC FUNCTIONS FOR ThO(g)

T K	CP CAL/K MOL	H-H0 CAL/MOL	S CAL/K MOL	-(G-H0)/T CAL/K MOL
298.15	7.47295	2105.99	57.3511	50.2775
300	7.4887	2122.22	57.3973	50.3213
400	7.86413	2891.77	59.6039	52.377
500	8.15122	3692.3	61.3913	54.0067
600	8.35275	4518.22	62.8942	55.3612
700	8.50132	5361.06	64.1955	56.5368
800	8.6214	6213.34	65.3387	57.567
900	8.73175	7085.82	66.3695	58.4853
1000	8.84455	7963.78	67.2863	59.3225
1100	8.96632	8854.24	68.1349	60.0856
1200	9.09925	9757.42	68.9207	60.7895
1300	9.24274	10674.4	69.6546	61.4435
1400	9.39457	11606.2	70.345	62.0549
1500	9.55197	12553.5	70.9985	62.6295
1600	9.71214	13516.7	71.6201	63.1721
1700	9.87268	14496.	72.2137	63.6866
1800	10.0317	15491.8	72.7825	64.1743
1900	10.1878	16502.2	73.329	64.6437
2000	10.3402	17528.7	73.8555	65.0912
2100	10.4884	18570.1	74.3636	65.5206
2200	10.6322	19626.2	74.8548	65.9338
2300	10.7718	20696.4	75.3305	66.332
2400	10.9071	21780.4	75.7916	66.7166
2500	11.0385	22877.7	76.2397	67.0886
2600	11.1663	23988.	76.6751	67.4489
2700	11.2905	25110.8	77.0988	67.7985
2800	11.4113	26246.	77.5115	68.138
2900	11.5289	27393.	77.914	68.4681
3000	11.6431	28551.6	78.3067	68.7895
3100	11.754	29721.5	78.6903	69.1027
3200	11.8614	30902.3	79.0651	69.4082
3300	11.9651	32093.6	79.4317	69.7063
3400	12.065	33295.2	79.7903	69.9976
3500	12.1608	34506.5	80.1414	70.2824
3600	12.2522	35727.2	80.4852	70.561
3700	12.339	36956.7	80.822	70.8337
3800	12.421	38194.8	81.1521	71.1008
3900	12.4981	39440.8	81.4757	71.3627
4000	12.5699	40694.2	81.793	71.6194
4100	12.6363	41954.5	82.1041	71.8713
4200	12.6973	43221.2	82.4093	72.1185
4300	12.7527	44493.7	82.7086	72.3613
4400	12.8026	45771.5	83.0023	72.5997
4500	12.8468	47054.	83.2905	72.834
4600	12.8855	48340.7	83.5732	73.8643
4700	12.9187	49630.9	83.8506	73.2908
4800	12.9466	50924.2	84.1228	73.5136
4900	12.9691	52220.	84.3899	73.7327
5000	12.9866	53517.7	84.652	73.9484
5100	12.9991	54817.	84.9092	74.1607
5200	13.0069	56117.3	85.1616	74.3698
5300	13.0102	57418.2	85.4093	74.5756
5400	13.0092	58719.1	85.6523	74.7784
5500	13.0040	60019.8	85.8909	74.9782
5600	12.9954	61319.7	86.125	75.1751
5700	12.9822	62618.6	86.3548	75.3691
5800	12.9672	63916.1	86.5804	75.5604
5900	12.9483	65211.8	86.8018	75.7489
6000	12.9267	66505.6	87.0191	75.9348

MOLECULAR WEIGHT= 248.037
MOLECULAR CONSTANTS ARE LISTED AS:
LEVEL,LE,XELE,YELE,BE,ALPHAE,DE,MULTIPLICITY,VPO

1	895.77	2.39	0	.320644	.001302	1.8330CE-7	1	0
2	864.1	2.31	0	.324413	.00122	1.8630CE-7	2	5305
3	840.4	2.4	0	.323044	.001294	1.566CCE-7	1	10600.8
4	842.8	2.18	0	.324973	.001299	1.942CCE-7	2	11125.1
5	835.1	2.39	0	.322455	.00125	1.931CCE-7	2	14490.
6	839.2	2.5	0	.32155	.0013	1.850CCE-7	2	15946.2
7	829.96	2.3	0	.32029	.001303	1.290CCE-7	1	16320.4
8	816.2	2.26	0	.319132	.00124	1.934CCE-7	2	17998
9	816.2	2.26	0	.321397	.00124	1.993395-7	1	18337.6
10	800.85	1.47	0	.3296	.00124	2.400CCE-7	2	19539.1
11	850.57	1.47	0	.32514	.00124	2.0590CE-7	2	21234.3
12	795.5	1.47	0	.318	.00124	2.000CCE-2	2	22635.7

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TABLE 4.   THERMODYNAMIC FUNCTIONS FOR $ThO_2(g)$

T	(G-H0)/T	(H-H0)/T	S	CP
298.15	-59.1581	9.9545	69.1126	11.3457
300	-59.2197	9.96313	69.1828	11.3625
400	-62.1487	10.4144	72.563	12.1255
500	-64.5163	10.8108	75.3271	12.6309
600	-66.5177	11.1436	77.6613	12.962
700	-68.2569	11.4203	79.6772	13.1847
800	-69.7974	11.6511	81.4485	13.3396
900	-71.1813	11.8452	83.0265	13.4509
1000	-72.438	12.0101	84.4481	13.5331
1100	-73.5895	12.1515	85.741	13.5954
1200	-74.6522	12.2739	86.9261	13.6437
1300	-75.639	12.3806	88.0198	13.6817
1400	-76.56	12.4748	89.0348	13.7123
1500	-77.4236	12.5582	89.9818	13.7371
1600	-78.2365	12.6325	90.869	13.7576
1700	-79.0044	12.6992	91.7036	13.7747
1800	-79.732	12.7594	92.4914	13.7891
1900	-80.4233	12.8139	93.2372	13.8013
2000	-81.0819	12.8636	93.9454	13.8118
2100	-81.7126	12.9089	94.6195	13.8208
2200	-82.3121	12.9506	95.2626	13.8287
2300	-82.8886	12.9889	95.8775	13.8355
2400	-83.4422	13.0243	96.4665	13.8416
2500	-83.9745	13.0571	97.0316	13.8469
2600	-84.4872	13.0876	97.5748	13.8517
2700	-84.9817	13.116	98.0977	13.8559
2800	-85.4592	13.1424	98.6016	13.8597
2900	-85.9208	13.1672	99.088	13.8631
3000	-86.3676	13.1905	99.5581	13.8662
3100	-86.8005	13.2123	100.013	13.869
3200	-87.2203	13.2329	100.453	13.8715
3300	-87.6278	13.2523	100.88	13.8738
3400	-88.0237	13.2706	101.294	13.8759
3500	-88.4086	13.2879	101.697	13.8778
3600	-88.7832	13.3043	102.087	13.8796
3700	-89.1479	13.3199	102.468	13.8812
3800	-89.5033	13.3347	102.838	13.8827
3900	-89.8499	13.3488	103.199	13.8841
4000	-90.188	13.3622	103.55	13.8854
4100	-90.5181	13.3749	103.893	13.8866
4200	-90.8406	13.3871	104.228	13.8877
4300	-91.1557	13.3986	104.554	13.8888
4400	-91.4639	13.4099	104.874	13.8897
4500	-91.7653	13.4206	105.186	13.8906
4600	-92.0604	13.4308	105.491	13.8915
4700	-92.3494	13.4406	105.79	13.8923
4800	-92.6324	13.4501	106.082	13.893
4900	-92.9099	13.4591	106.369	13.8937
5000	-93.1819	13.4678	106.65	13.8944
5100	-93.4486	13.4762	106.925	13.895
5200	-93.7104	13.4842	107.195	13.8956
5300	-93.9673	13.492	107.459	13.8961
5400	-94.2196	13.4995	107.719	13.8966
5500	-94.4674	13.5067	107.974	13.8971
5600	-94.7109	13.5137	108.224	13.8976
5700	-94.95	13.5204	108.47	13.898
5800	-95.1852	13.5269	108.712	13.8985
5900	-95.4165	13.5332	108.95	13.8989
6000	-95.644	13.5393	109.183	13.8992

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FREQ 787.2 MULT 1
FREQ 735.5 MULT 1
FREQ 81 MULT 1
MOLECULAR WEIGHT 264.037
SYMMETRY 2
MOMENTS 24.863   69.708   94.571
END OF RUN
```

TABLE 5. THERMODYNAMIC FUNCTIONS FOR ThO_2(g)

T	(G-H0)/T	(H-H0)/T	S	CP
298.15	-58.6895	9.7791?	68.2677	11.311?
300	-58.55	9.78769	68.3377	11.3?0?
400	-61.6341	10.2765	71.7195	12.1060
500	-63.7738	10.6973	74.4711	12.6186
600	-65.7561	11.2074	76.8936	12.053?
700	-67.6915	11.3368	78.0100	13.178?
800	-69.0115	11.5773	80.5688	13.3360
900	-70.3071	11.7791	82.1668	13.6677
1000	-71.6372	11.9503	83.5875	13.53?
1100	-72.7939	12.2969	84.8801	13.5000
1200	-73.8616	12.2936	86.065	13.6015
1300	-74.8243	12.3342	87.1595	13.6700
1400	-75.742	12.4315	88.1735	13.7187
1500	-76.6026	12.5176	89.1293	13.7358
1600	-77.413	12.5944	90.0376	13.7564
1700	-78.1786	12.6633	90.860	13.7736
1800	-78.9042	12.7254	91.6297	13.7881
1900	-79.5930	12.7817	92.3755	13.0006
2000	-80.2507	12.8329	93.0036	13.811
2100	-80.878	12.8707	93.7577	13.8201
2200	-81.6782	12.9026	94.60?	13.828
2300	-82.0535	12.9621	95.0156	13.?35
2400	-82.6859	12.9996	95.6046	13.641
2500	-83.1373	13.0320	96.1697	13.846?
2600	-83.669	13.0630	96.7120	13.8510
2700	-84.1406	13.0931	97.2357	13.8555
2800	-84.6193	13.1206	97.7307	13.8503
2900	-85.0801	13.1659	98.2261	13.8607
3000	-85.5262	13.1699	98.6961	13.8650
3100	-85.9584	13.1926	99.1538	13.6686
3200	-86.3716	13.2135	99.6011	13.8710
3300	-86.7865	13.2336	100.010	13.8725
3400	-87.1709	13.2526	100.620	13.8756
3500	-87.5643	13.2709	100.836	13.8776
3600	-87.9383	13.2871	101.095	13.8706
3700	-88.3026	13.3231	101.626	13.881
3800	-88.6576	13.3183	101.976	13.8905
3900	-89.0037	13.3329	102.337	13.8930
4000	-89.3615	13.3466	102.680	13.8650
4100	-89.6712	13.3598	103.021	13.8967
4200	-89.9533	13.3723	103.366	13.8975
4300	-90.3281	13.3903	103.699	13.8986
4400	-90.6159	13.3958	104.012	13.8906
4500	-90.9171	13.0368	104.320	13.8035
4600	-91.2119	13.0173	104.620	13.8012
4700	-91.5025	13.0070	104.908	13.8901
4800	-91.7833	13.0371	105.20	13.8000
4900	-92.0605	13.0066	105.507	11.8036
5000	-92.3302	13.0553	105.788	13.8060
5100	-92.5008	13.060	106.063	13.8060
5200	-92.8603	13.6722	106.233	13.8055
5300	-93.117	13.6832	106.507	13.806
5400	-93.362	13.6979	106.767	13.5066
5500	-93.6166	13.6057	107.119	13.607
5600	-93.6508	13.5326	107.369	13.8076
5700	-94.0090	13.5205	107.620	13.8979
5800	-94.3239	13.5162	107.95	13.8984
5900	-92.0605	13.4466	105.507	13.8036
6000	-94.7923	13.5089	108.391	13.8901

FREQ 787.0 MULT 1
FREQ 735.5 MULT 1
FREQ 125 MULT 1
MOLECULAR WEIGHT 264.037
SYMMETRY 2
MOMENTS 24.863   69.708   94.571
END OF RUN

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